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Synthesis of hydroxyapatite at low temperature

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Abstract : $(NH_4)_2HPO_4$ and $CaCl_2$ were used as the P and Ca precursors for the synthesis of pure, stable, stoichiometric, crystalline hydroxyapatite at low temperature The synthesized sample thus obtained was studied using energy dispersive X-ray fluorescence, X-ray diffraction, and thermogravimetric analysis. X-Ray diffraction analysis showed different phases of hydroxyapatite, energy dispersive X-ray fluorescence analysis confirmed the Ca/P, while thermogravimetric analysis showed the stability of the synthesized hydroxyapatite

Keywords : Crystal growth, EDXRF, XRD, TGA.

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1. Introduction

Bioactive apatite, such as calcium hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$, HAp], is widely used as implant or repair materials for bone and because of its similarity in chemical composition to the inorganic matrix of bone and teeth. Its bioactivity leads to bonding directly to the bone tissue without any fibrous encapsulation [1]. Recently, nanoscale materials have been prepared and received great interest because they are expected to play a key role in basic scientific research and fabricating nanodevices with novel optical, electric and magnetic properties. Various preparation methods towards diverse nanomaterials, including templating direction, solution-based solvothermal or hydrothermal treatment and sol-gel method have been extensively developed [2]. A number of more soluble calcium phosphate phases such as tricalcium phosphate, octacalcium phosphate and dicalcium phosphate dihydrate may also be formed in supersaturated calcium phosphate solutions at ambient temperatures. In several cases, the ionic activity of calcium and phosphate ions in biological fluids is sufficiently low so as to preclude the formation of any precursor phases other than HAp [3]. Also, the control of sintering behavior of HAp powder is very important. For instance, highly dense HAp would be desirable to prevent the preparation of human fluid into the interfacial area between HAp film and Ti-alloys in the hip joint replacements, while porous HAp would be needed for

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the broken bone replacements in which the intergrowth of natural and artificial bones occurs and strong bond between them can be readily attained [4]. The mineral of teeth and bones consists of HAp, with some ion substitution. It is well known that apatitic mineral in bone consists of very small plate-like crystals and that pure HAp crystals are larger and needle-like in shape. An understanding of the processes of formation, growth and dissolution of pure HAp will nevertheless assist the explanation of the influence of other ions such as carbonate and sodium found in biological apatitic mineral [5]. Numerous methods for HAp synthesis have been reported in the literature, including solid state reaction, hydrothermal growth, precipitation and hydrolysis of the acid calcium phosphate modifications. Due to the low cost and simplicity of the procedure, there is considerable interest in the hydroxyapatite synthesis from aqueous solutions. However, most of the apatites obtained in this way are reported as nonstoichiometric [6]. But, the present study concentrates on the formation of hydroxyapatite in a very simple way by wet chemical synthesis. It is known to be biocompatible, bioactive *i.e.* ability to form a direct chemical bond with living tissues, osteoconductive, non-toxic, non inflammatory and non-immunogenic agent.

2. Experimental procedures

2.1. Synthesis of hydroxyapatite :

The hydroxyapatite was obtained by using analytical grade $(NH_4)_2HPO_4$ and $CaCl_2$. 0.3 M aqueous solution of $(NH_4)_2HPO_4$ was added to 0.5 M aqueous solution of $CaCl_2$ drop by drop. While adding $(NH_4)_2HPO_4$, the temperature of $CaCl_2$ solution was maintained at 55°C. The pH of the resulting solution was maintained to 9 by adding concentrated NH_4OH drop by drop. Then the solution was stirred for 2 hours at 55°C at 400 rpm. The resulting solution was again stirred for 15 hours at 400 rpm in room temperature. The solution was filtered with Whatmann filter paper and washed with de-ionised water repeatedly for 5 to 6 times. The final precipitate was centrifuged at 9000 rpm for 8 minutes. Then the precipitate was dried at 50°C until complete removal of water particles.

2.2. Energy dispersive X-ray fluorescence (EDXRF) :

The EDXRF system at Institute of Physics, Bhubaneswar has been used for detecting the presence of Ca and P in the synthesized hydroxyapatite and to calculate the Ca/P ratio. It incorporates a low power air-cooled X-ray tube (50-watt) as an excitation source with tri-axial geometry [7]. The X-ray tube was operated at 35 kV and 0.6 mA. The K-characteristic X-rays of molybdenum were used to excite the characteristic X-rays of elements present in all the samples, which were then collected using a Si (Li) detector and the spectrum was recorded by using a PC-based multi-channel analyzer [8]. The photo-peak areas in each spectrum were evaluated using the computer program AXIL [9] supplied by International Atomic Energy Agency (IAEA).

2 3 X-Ray diffraction (XRD)

XRD technique was used to determine different phases of hydroxyapatite The XRD pattern of hydroxyapatite is shown in Figure 2 It is evident from the figure that, 18

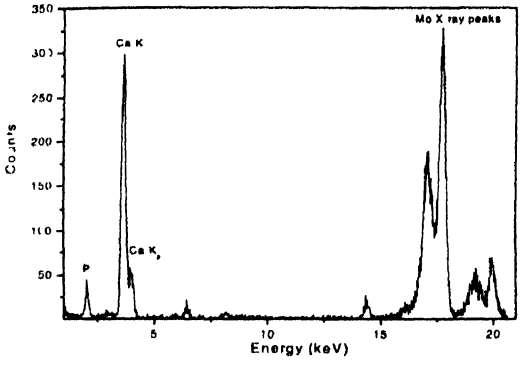

Figure 1. EDXRF spectrum of hydroxyapatite

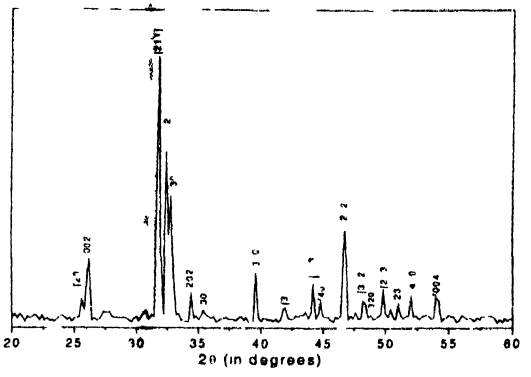

Figure 2. XRD pattern of hydroxyapatite

different crystallographic phases of hydroxyapatite were identified using PCPDFWIN, V1 3 (JCPDS 1997) [10] Peak search was carried out using Philips X'Pert Graphics software The XRD patterns were recorded with a step size of 0 02° on a 20–60° range with a scanning rate of 2°/min Line focus Ni-filtered CuK_α radiation from an X-ray tube (operated at 40 kV and 30 mA) was collimated through soller slit of 0 04 radian, fixed divergence slit of 1° and mask (5 mm) before getting it diffracted from the sample

2 4 Thermogravimetric analysis (TGA)

Shimadzu thermal analyzer [11] at Utkal University, Bhubaneswar, India was used for the TGA of powdered samples The weight loss of the sample was monitored under air atmosphere Each sample was heated under air atmosphere at a linear heating rate of 10°C min^{-1} from 35°C to 600°C The TGA spectrum of HAp is shown in Figure 3

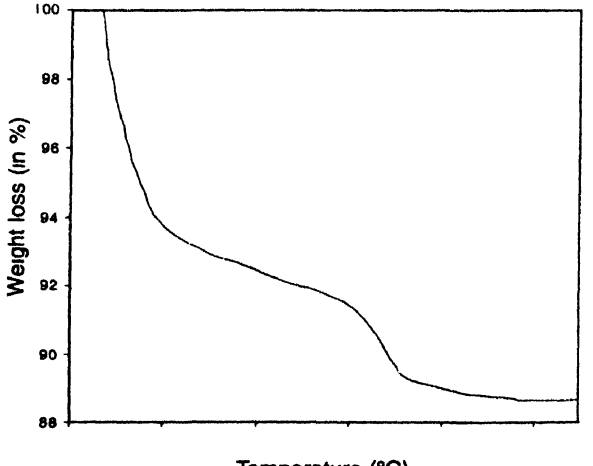

Figure 3. TGA spectrum of hydroxyapatite

3. Results and conclusion

From the EDXRF analysis, it was found that the Ca/P ratio of the synthesized sample is 1.66 which is in close agreement with the Ca/P ratio of hydroxyapatite *i.e.* 1.6667. Even though utmost care was taken to avoid contaminants, few ppm of contaminants is present in the synthesized sample which may be due to the de-ionised Millipore water. The XRD pattern confirmed different phases of hydroxyapatite. The spectrum is in close agreement with the standard PDF No. : 74-0566 having hexagonal structure with space group $P6_3/m$ where $\alpha = \beta = 90°$ and $\gamma = 120°$. Thermogravimetric analysis of the as-prepared HAp powder in the temperature range of 35–550°C confirmed results of other characterization. The TGA (Figure 3) showed a two-stage weight loss at the temperature range of 35–130°C and 270–400°C. In the first stage, a sharp 7% weight loss was observed, indicating the evaporation of adsorbed water. The second stage showed a 3% weight loss due to the loss of adsorbed and lattice water. However, there was no further weight loss on heating up to 550°C, which indicates the high thermal stability of the sample. The XRD and EDXRF studies confirmed the synthesized sample to be hydroxyapatite, while TG-DTG study confirmed its high thermal stability.

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